NOVEL MESOGENS

Priority Data

The present application claims the benefit of the following provisional applications, all filed January 23, 2001: Serial No. 60/263,387; Serial No. 60/263,392; Serial No. 60/263,388.

Government Rights Clause

The U. S. government has certain rights in this invention pursuant to grant number NIDCR 1 P01 DE11688.

Field of the Invention

The invention relates to novel platform molecules, polymerizable mesogens, dimers, and diluents for photocurable resins.

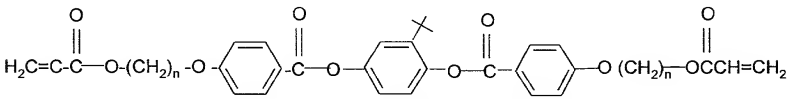
Background of the Invention

Photocurable resins which are transparent or translucent, radioopaque, have good workability, and have good mechanical strength and stability are useful in medical, dental, adhesive, and stereolithographic applications.

Low polymerization shrinkage is an important property for such resins. In dental applications, the phrase "zero polymerization shrinkage" typically means that the stresses accumulated during curing do not debond the dentin-restorative interface or fracture the tooth or restorative, which can result in marginal leakage and microbial attack of the tooth. Low polymerization shrinkage also is important to achieve accurate reproduction of photolithographic imprints and in producing optical elements.

Another advantageous property for such resins is maintenance of a liquid crystalline state during processing. For comfort in dental applications, the resin

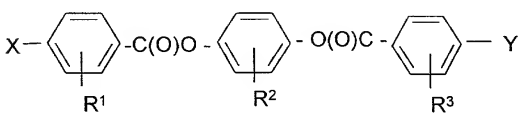
should be curable at "room temperature," defined herein as typical ambient temperatures up to body temperature. Preferred curing temperatures are from about 20 °C to about 37 °C. Mesogens which have been found to polymerize in a relatively stable manner at such temperatures are bis 1,4 [4'-(6'-methacryloxyhexyloxy) benzoyloxy] t-butylphenylene mesogens and their structural derivatives. These mesogens have the following general structure:



Known synthetic methods for producing these mesogens are costly and have relatively low yields. New synthetic methods and new methods and compositions for controlling rheology of these photocurable resins are needed.

Summary of the Invention

Mesogens are provided having the following general formula:



wherein

X and Y independently are selected from the group consisting of terminal functionalities and polymerizable groups, provided that, when X and Y both are polymerizable groups, X and Y are other than bis- vinyl terminated groups;

R^2 is a bulky organic group having a bulk greater than R^1 and R^3 whereby, when both X and Y are polymerizable groups, said bulk is adapted to provide sufficient steric hindrance to achieve a nematic state at room temperature while

suppressing crystallinity at room temperature, thereby providing effective rheology and workability at room temperature; and

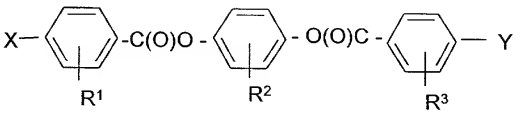
R^1 and R^3 are selected from groups less bulky than R^2 adapted to maintain said nematic state.

Detailed Description of the Invention

The application provides novel platform molecules, novel polymerizable mesogens, novel methods for using the platform molecules, and novel intermediates and synthetic pathways for making the platform molecules and polymerizable mesogens.

The Mesogens

The mesogens have the following general structure (1):



wherein X and Y are selected from the group consisting of terminal functionalities and polymerizable groups. In platform molecules, X and Y are terminal functionalities. In polymerizable mesogens, X and Y are polymerizable groups. Terminal functionalities and polymerizable groups are further defined below; and,

R^2 is a bulky organic group having a bulk greater than R^1 and R^3 whereby, when X and Y are both polymerizable groups, said bulk is adapted to provide sufficient steric hindrance to achieve a nematic state at room temperature while suppressing crystallinity at room temperature. The result is effective rheology and workability at room temperature. Suitable R^2 groups generate

asymmetry in the packing of the molecules, and include, but are not necessarily limited to alkyl groups having from about 1 to 6 carbon atoms and aryl groups. Preferred R^2 groups include, but are not necessarily limited to alkyl groups having from about 1 to about 4 carbon atoms and phenyl groups. More preferred R^2 groups are methyl groups, t-butyl groups, isopropyl groups, secondary butyl groups, and phenyl groups. Most preferred R^2 groups are methyl groups and t-butyl groups; and

R^1 and R^3 are selected from groups less bulky than R^2, preferably selected from the group consisting of hydrogen atoms and methyl groups, depending upon the relative bulk of R^1, R^3, and R^2.

As used herein, the phrase "terminal functionalities" refers to X and Y where the referenced molecules are platform molecules. "Terminal functionalities" are defined as protective groups and precursors to polymerizable groups, which generally comprise functionalities that readily react with "polymerizable groups" to form reactive ends. Suitable terminal functionalities independently are selected from the group consisting of hydroxyl groups, amino groups, sulfhydryl groups, halogen atoms, and "spacer groups", defined herein as selected from the group consisting of $H\text{-}(CH_2)_n\text{-}O\text{-}$ groups, $Cl(CH_2)_n\text{-}O\text{-}$ groups, $Br(CH_2)_n\text{-}O\text{-}$ groups, $I(CH_2)_n\text{-}O\text{-}$, wherein n is from about 2 to about 12, preferably from about 2 to about 9, more preferably from about 2 to about 6, and most preferably 6, and the CH_2 groups independently can be substituted by oxygen, sulfur, or an ester group; provided that at least 2 carbon atoms separate said oxygen or said ester group. Most preferred terminal functionalities are hydroxyl groups.

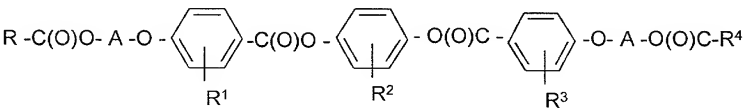
Where the mesogen is a polymerizable mesogen, X and/or Y are "polymerizable groups," defined as groups that may be polymerized by nucleophilic addition, free radical polymerization, or a combination thereof. Preferred polymerizable groups are polymerizable by Michael addition. Michael addition requires the addition of a nucleophile and an electron deficient alkene. Groups suitable for polymerization by Michael addition include but are not necessarily limited to the examples found in A. Michael, *J. Prakt. Chem. [2] 35, 349 (1887)*; R. Connor and W. R. McClelland, *J. Org. Chem.*, **3**, 570 (1938); and C. R. Hauser, M. T. Tetenbaum, *J. Org. Chem.*, **23**, 1146 (1959), all of which are incorporated by reference herein.

Examples of suitable polymerizable groups include, but are not necessarily limited to substituted and unsubstituted alkenyl ester groups comprising a polymerizable unsaturated carbon-carbon bond, wherein said alkenyl group has from about 2 to about 12 carbon atoms, preferably from about 2 to about 9 carbon atoms, more preferably from about 2 to about 6 carbon atoms. In one embodiment, said substituted alkenyl ester groups comprise at least one halogen atom selected from the group consisting of chorine atoms, bromine atoms, and iodine atoms. Preferred alkenyl esters are acryloyloxy alkoxy groups and methacryloyloxy alkoxy groups. More preferred polymerizable groups include, but are not necessarily limited to cinnamoyloxy groups, acryloyloxy groups, methacryloxy groups, as well as thioalkyloxy groups, acryloyloxy alkoxy groups, and methacryloyloxy alkoxy groups comprising an alkyl moiety having from about 2 to about 12 carbon atoms, preferably about 6 carbon atoms, said alkyl moieties comprising CH_2 groups which independently can be substituted by oxygen, sulfur, or an ester group; provided that at least 2 carbon atoms separate said oxygen or said ester group. Because assymetry

suppresses crystallinity while maintaining a nematic state, it is preferred for X and Y to be different groups.

Certain bis-acryloyloxy alkyloxy and bismethacryloyloxy alkyloxy polymerizable mesogens are the subject of a separate patent based on a copending application, U.S. Patent No. 6,258,974. Applicant here claims mesogens other than those described in U.S. Patent No. 6,258,974.

Most preferred polymerizable mesogens are bis 1,4 [4'-(6'-(R,R^4)-oxy-A-oxy)benzoyloxy] R^2-phenylene mesogens. These mesogens have the following general structure:



Referring to Fig. 1, X and Y are replaced by polymerizable groups wherein:

A is selected from the group consisting of alkyl groups and methyl-substituted alkyl groups having from about 2 to about 12 carbon atoms, preferably having from about 2 to about 9 carbon atoms, more preferably having from about 2 to about 6 carbon atoms, and most preferably having about 6 carbon atoms; and

R and R^4 are polymerizable groups, including but not necessarily limited to nucleophiles and groups comprising at least one electron deficient alkene. Suitable nucleophiles include, but are not necessarily limited to ester groups, organic acid groups, amine groups, hydroxyl groups, and sulfhydryl groups. More preferred polymerizable groups comprise electron deficient alkenes. Suitable electron deficient alkenes independently are selected from the group

consisting of substituted and unsubstituted alkenyl ester groups comprising a polymerizable unsaturated carbon-carbon bond, wherein said alkenyl group has from about 2 to about 12 carbon atoms, preferably about 6 carbon atoms. In one embodiment, said substituted alkenyl ester groups comprise a halogen atom selected from the group consisting of chorine atoms, bromine atoms, and iodine atoms. Preferred alkenyl esters are acryloyl groups and methacryloyl groups. Again, because assymetry suppresses crystallinity while maintaining a nematic state, it is preferred for X and Y to be different groups. One end of a polymerizable mesogen also may comprise a bridging agent, making the mesogen a "dimer," discussed in more detail below. In the case of dimers, R^2 may also be a hydrogen, a halogen, or another a group less bulky than a methyl group, due to the inherent asymmetry of the dimer molecule.

In a preferred embodiment, R^2 is selected from the group consisting of a methyl group and a t-butyl group, A is a hexyl group, and one of R and R^4 is selected from the group consisting of an acryloyl group and a methacryloyl group.

In a preferred embodiment, a proportion of X and/or Y (or R and/or R^4) comprises a crystallization retardant. A "crystallization retardant" is defined as a substituent that retards crystallization of the monomers without suppressing the $T_{n->isotropic}$ (the nematic to isotropic transition temperature). The proportion of X and/or Y (or R and/or R^4) that comprises a crystallization retardant preferably is sufficient to suppress crystallinity of the mesogenic material, particularly at room temperature for dental applications, and to maintain flowability of the mesogenic material under the particular processing conditions. Suitable crystallization retardants include, but are not necessarily limited to halogen atoms. Exemplary halogen atoms are chlorine,

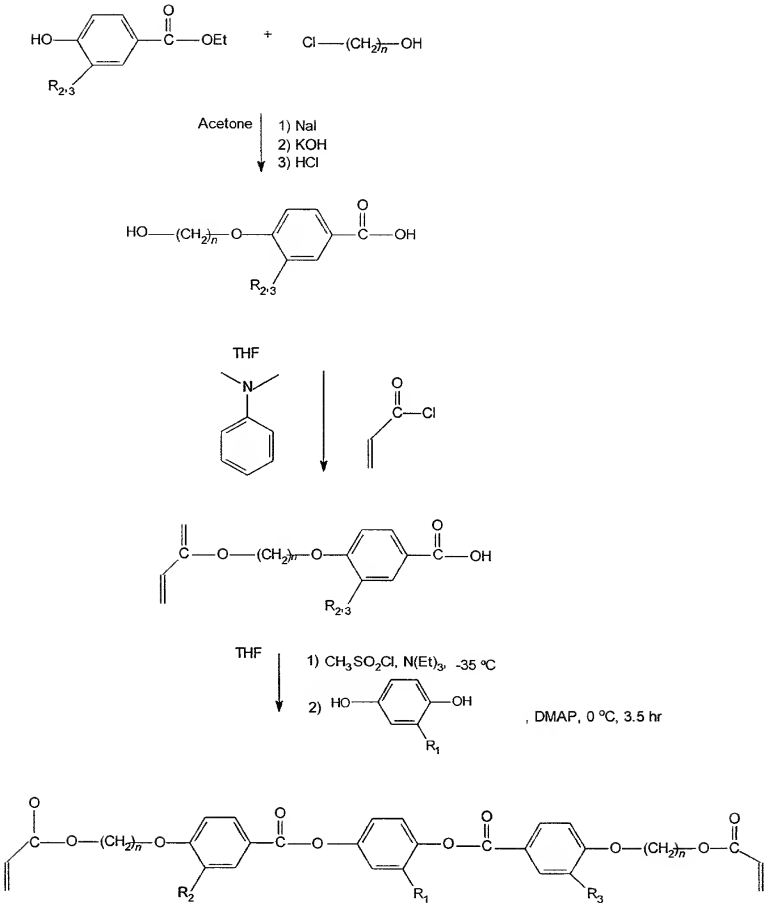
bromine, and iodine, preferably chlorine. Typically, the proportion of the crystallization retardant required is about 3-50 mole%, more preferably 10-15 mole%, and most preferably about 14 mole% or less.

Mesomers of higher temperature nematic stability are "mesogenic dimers," formed by reacting X and Y with opposite ends of a bridging agent. Examples of suitable bridging agents include, but are not necessarily limited to dicarboxylic acids (preferably α,ω-carboxylic acids) having from about 4 to about 12 carbon atoms, preferably from about 6 to about 10 carbon atoms, and oligodialkylsiloxanes preferably comprising alkyl groups having from about 1 to about 3 carbon atoms, most preferably methyl groups. When the mesomer is a dimer or another structure comprising components that inherently interfere with crystallization at room temperature, R^2 need not have a bulk greater than R^1 and R^3. Hence, R^2 may be hydrogen, a halogen atom, or another substituent having lesser bulk than a methylene group.

Depending on the sample preparation, the volumetric photopolymerization shrinkage of these materials at room temperature varies from about 0.9 to about 1.7%, which is a factor of 6-4X improvement over commercially available blends containing 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenylene] propane ("bis-GMA"). Preferably, the polymerizable mesogens exhibit "low polymerization shrinkage," defined herein as about 3 vol.% change or less, preferably about 2 vol.% change or less.

New Synthetic Pathways to Make the Mesogens

In the past, polymerizable mesogens having the foregoing structure were synthesized by a multistep process ("Scheme 1"), as shown below:


Acetone
1) NaI
2) KOH
3) HCl
THF
THF
1) CH_3SO_2Cl, $N(Et)_3$, -35 °C
2)
, DMAP, 0 °C, 3.5 hr

Scheme 1.

In Scheme 1, molecular ends containing the outer aromatic groups and the alkyl groups were produced first and then coupled to the central aromatic group by diaryl ester bonds. Specifically, the alkali phenoxide salt of p-hydroxybenzoic acid-ethyl ester nucleophile attacked the 6-hydroxy 1-chloro hexane with the aid of iodide catalyst to produce the 6-hydroxyhexyloxybenzoic acid (after hydrolysis of the ethyl ester) by a procedure that yielded at best 70% product. Although rather straightforward, the commercial potential of this synthesis has been limited by the use of the 6-hydroxy 1-chlorohexane. The reaction is run in acetone over several days and requires significant workup. The reaction also produces only about a 40% overall yield, at best, and requires column separation to separate monosubstituted from disubstituted material

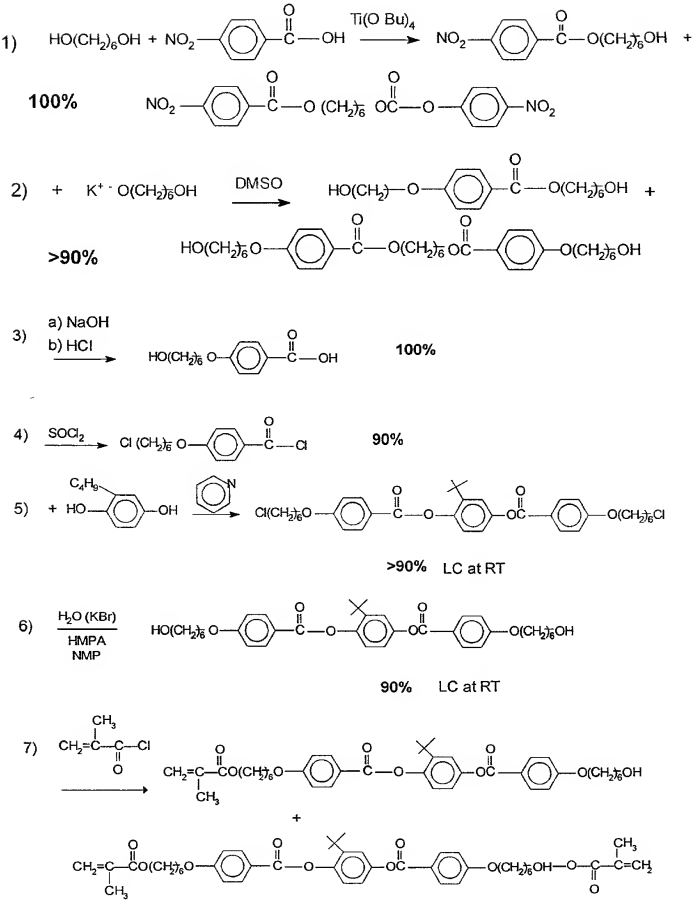
New synthetic pathways are provided are provided that use relatively low cost materials to synthesize a central aromatic component comprising end groups that are easily reacted with the desired polymerizable groups. The methods are qualitative, produce high yields, the products are easily purified (preferably by crystallization), and many of the products are more stable than bisalkenes, which must be stabilized against polymerization.

Brief Summary of the Processes

Reactive groups on a phenylene ring at para-positions (preferably hydroxyl groups) form ester linkages with one of two reactive groups in para-positions on two other phenylene rings. The result is three-ring platform mesogens having terminal functionalities. One or both of the terminal functionalities may be coupled with polymerizable groups, preferably a nucleophile and/or an electron deficient alkene-containing group, to produce polymerizable mesogens.

-Preparation of Molecular Ends and Coupling to Central Aromatic Group

In a first embodiment (Scheme 2), the molecular ends of the mesogen (outer aromatic and alkyl groups) are prepared and coupled to the central aromatic group by diaryl ester bonds. This synthetic pathway is illustrated and described in detail below:



Scheme 2.

Exemplary "platform molecules" are illustrated in (6), above.

To summarize Scheme 2, bis 1,4 [4"-(6'-chloroalkyloxy) benzoyloxy] R^{2-} phenylene, preferably bis 1,4 [4"-(6'-chlorohexyloxy) benzoyloxy] t-butylphenylene,

is converted to the analogous bis ω-hydroxy or ω-hydroxy chloro compound. The hydroxy- compound (the platform molecule) may be terminated with one or more polymerizable groups. Preferred polymerizable groups are nucleophilic and electron deficient groups, most preferably independently selected from the group consisting of acryloyl groups, methacryloyl groups, and cinnamoyl groups.

More particularly:

(1) 4-nitrobenzoic acid is dissolved in an excess of the desired 1,6-dihydroalkane, preferably 1.6-dihydroxyhexane, in the presence of a suitable esterification catalyst. Suitable catalysts include, but are not necessarily limited to titanium alkoxides, tin alkoxides, sulfonic acid, and the like. A preferred catalyst is $Ti(OBu)_4$. The dissolution occurs at atmospheric pressure at a temperature of from about 120 °C to about 140 °C, with stirring. If excess alcohol is used, the majority product is the 6-hydroxyalkyl ester of 4-nitrobenzoic acid plus some bis 1,6-(4-nitrobenzoyloxy) alkane, preferably 1,6-(4-nitrobenzoyloxy) hexane. The byproduct water is removed using suitable means, preferably under vacuum during the course of the reaction.

(2) One or more suitable solvents are added to the reaction mixture, along with alkali salts of diols. Suitable solvents include, but are not necessarily limited to aprotic solvents in which nucleophilic attack is preferred. Examples include, but are not necessarily limited to dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), dimethyl acetamide (DMAC), hexamethyl phosphonamide (HMPA). A preferred solvent is dimethylsulfoxide (DMSO), which is environmentally safe and relatively inexpensive. Suitable salts comprise cations effective to displace hydrogen and to produce the mono-cation salt of the alkanediol, preferably the nucleophilic

monosodium salt of hexanediol, in the presence of excess alkyldiol, preferably hexanediol. Preferred salts include, but are not necessarily limited to NaH or $KOBu^t$. The salt of the alkane diol, preferably hexane diol, then displaces the activated nitro group to produce 4-(1-hydroxyalkyloxy)benzoic acid (1-hydroxyalkyl ester) and some of the dimeric compound. A preferred product is 4-(1-hydroxyhexyloxy)benzoic acid (1-hydroxyhexyl ester) and some of the dimeric compound. See N.Kornblum et al., J. Org. Chem., **41**(9), 1560 (1976) , incorporated herein by reference (nucleophilic displacement of nitro- group).

(3) The mixture from (2) is diluted with an aqueous base and heated to completely cleave the aryl-alkyl ester to produce the desired 4-(6'-hydroxyakyloxy)benzoic acid by precipitation subsequent to acidification. Suitable aqueous bases include, but are not necessarily limited to inorganic bases, a preferred base being aqueous sodium hydroxide. Suitable acids include, but are not necessarily limited to inorganic acids, a preferred acid being hydrochloric acid. In a preferred embodiment, 4-(1-hydroxyhexyloxy)benzoic acid (1-hydroxyhexyl ester) is diluted with aqueous sodium hydroxide and then acidified using hydrochloric acid to produce 4-(6'-hydroxyhexyloxy)benzoic acid. The supernatent contains sodium chloride and nitrite, which can be removed and recovered by vacuum evaporation of the solvent. In a preferred embodiment, the solvents evaporated are DMSO, hexanediol and water, which may be discarded. DMSO and hexanediol can be recovered from the water phase by known distillation procedures.

(4) In a preferred embodiment, for small scale procedures, a quantitative conversion of the 4-(6'-hydroxyalkyloxybenzoic acid to 4-(6'-chloroalkyloxy) benzoyl chloride is accomplished by mixing with thionyl chloride diluted in a suitable solvent,

preferably toluene, in the presence of pyridine base. In a preferred embodiment, 4-(6'-hydroxyhexyloxy)benzoic acid is converted to 4-(6'-chlorohexyloxy)benzoyl chloride in this manner. On a larger scale, the foregoing reaction is implemented with simple addition of $SOCl_2$ and venting of the byproduct SO_2 and HCl.

(5) The highly reactive 4-(6'-chloroakyl)benzoyl chloride is coupled to a hydroquinone bearing the desired bulky group, R^2. In a preferred embodiment, 4-(6'-chlorohexyl)benzoyl chloride is mixed at room temperature with t-butyl hydroquinone in ether with pyridine, used as catalyst and as a base to take up released HCl, to form bis 1,4 [4"-(6'-hydroxyhexyloxy) benzoyloxy] t-butylphenylene. The reaction is quantitative and produces a high yield of the desired product. In addition, the bis 1,4 [4"-(6'-chloroalkloxy) benzoyloxy] R^2- phenylene, preferably bis 1,4 [4"-(6'-chlorohexyloxy) benzoyloxy] t-butyl phenylene, is easily purified from the reaction mixture by crystallization. In addition, the bischlorocompound is stable and need not be stabilized against polymerization (as must bis-alkene compounds).

(6) The bischlorocompound is hydrolyzed to the platform molecule, preferably bis 1,4 [4"-(6'-chlorohexyloxy)benzoyloxy] t-butylphenylene, by simple heating in an aprotic solvent in the presence of water and potassium bromide [R.O. Hutchins and I.M. Taffer, J.Org. Chem., **48**, 1360 (1983)]. Again, the reaction is quantitative with the product being purified by recrystallization. The reaction can be stopped at intermediate times to produce any desired mixture of monofunctional and difunctional alcohol molecules. In addition, the chloro-terminated molecules can be converted to the more reactive iodo-terminated species by simple exchange with NaI in acetone.

(7) The dialcohol or mixed alcohol/alkyl chloride is easily reacted with one or more polymerizable groups, preferably Michael addition reactants. In a preferred embodiment, one or more of the dialcohol ends is reacted with alkenyl chlorides to form reactive alkenyl esters, which can have any ratio of alkenyl ester, halide, or alcohol termini. The ratio can be adjusted to adjust the crosslink density and the liquid crystal transition temperatures.

Selective Ether Cleavage

In a preferred embodiment, 4-alkoxy benzoyl chloride, preferably commercially available 4-methoxy benzoyl chloride, is reacted with a hydroquinone substituted with a desired R^2 group to produce the corresponding aromatic ester, bis 1,4 [4-alkoxybenzolyoxy] phenylene, preferably bis 1,4 [4-methoxybenzolyoxy] phenylene. The reaction takes place in the presence of an appropriate HCl scavenger and solvent. Suitable HCl scavengers include, but are not necessarily limited to aromatic and aliphatic amines, with a preferred HCl scavenger being pyridine. The pyridine also may be used in combination with a trialkyl amines having from about 2-4 carbon atoms, preferably triethyl amine.

In a second "step," the alkoxy group is cleaved to result in a reactive hydroxyl group while leaving the aromatic ester and thus the triaromatic mesogen structure intact. See M. Node et al., J. Org. Chem., **45**, 4275 (1980)] (Figure 7a), incorporated herein by reference. Node suggests that the methyl ether of bis 1,4 [4-methoxybenzolyoxy] phenylene can be selectively cleaved in the presence of a nucleophile, preferably a thiol, and a Lewis acid, such as aluminum chloride, to produce bis 1,4 [4-hydroxybenzoyloxy] phenylene. [See M. Node et al., J. Org. Chem., **45**, 4275 (1980)] ("Node"), incorporated herein by reference. However, Node

describes cleaving methyl ethers in the presence of aliphatic esters--not in the presence of aromatic esters. In initial experiments using the conditions described in Node, the more unstable aromatic esters underwent significant ester cleavage because the product complex remained in solution where additional reaction can occur.

Surprisingly, selective cleavage of the aliphatic ether in the presence of the aromatic esters was induced at low temperatures using much higher methyl ether concentrations than those described in Node. Using high concentrations of the ether and much lower concentrations of the nucleophile induced a "complex"-- containing the dihydroxy product with intact aromatic ester bonds--to precipitate from the reaction mixture at short reaction times as the complex was formed. The precipitated complex decomposed to the desired dihydroxy compound by reacting the complex with water and/or alcohol.

Suitable ethers for use in the reaction include, but are not necessarily limited to alkyl ethers, having from about 1 to about 8, preferably 1 to 4 carbon atoms. A most preferred ether is methyl ether. Suitable nucleophiles for use in the reaction include, but are not necessarily limited to aliphatic thiols. Preferred nucleophiles are liquid alkanethiols, which typically have 11 carbon atoms or less. A most preferred nucleophile is ethane thiol.

Preferably, a minimum amount of thiol is used to dissolve aluminum chloride in the presence of the ether and a solvent. A most preferred embodiment uses at least 1 mole of thiol per mole of alkyl ether, preferably 2 moles of thiol per mole of alkyl ether. A most preferred embodiment uses 7 mmol of the methyl ether per ml of ethane thiol.

The aluminum chloride to ether ratio should be 4:1 or more, as this appears to

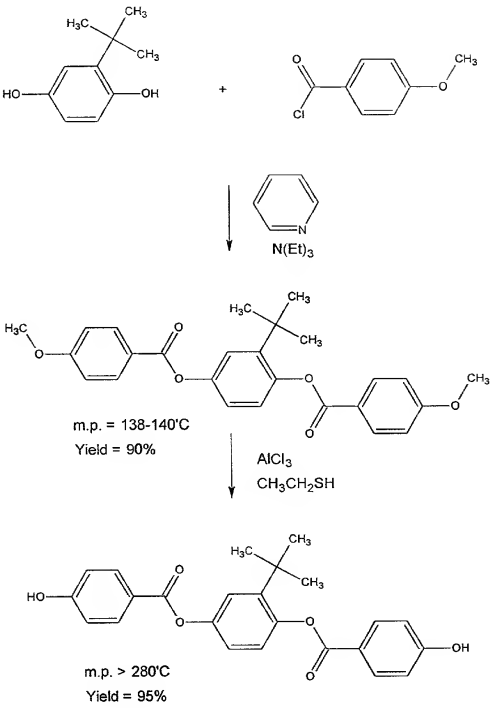
be the ratio needed for complexation. At ratios of aluminum chloride to thiol of above 5, more of the complex will stay in the solution before saturation occurs thus resulting in aromatic ester cleavage and reduced yield. The use of less aluminum chloride will result in an incomplete cleavage of the methyl ether. The use of more aluminum chloride, in excess of 4 to 1, has shown no effect in increasing the reaction rate, but slight excesses such as 4.5 to 1 can compensate for residual water in the system.

Suitable solvents for use in the reaction are halogenated solvents, preferably chlorinated solvents, most preferably dichloromethane. The solvent concentration can range from a molar excess of from about 3 to about 7, preferably about 5 or more, in relation to the nucleophile (thiol), as needed to keep the solution in a slurry as precipitate forms. However, dichloromethane above a 5 molar excess should be added slowly as the reaction proceeds since high initial concentration of the methylene chloride will hinder the reaction rate.

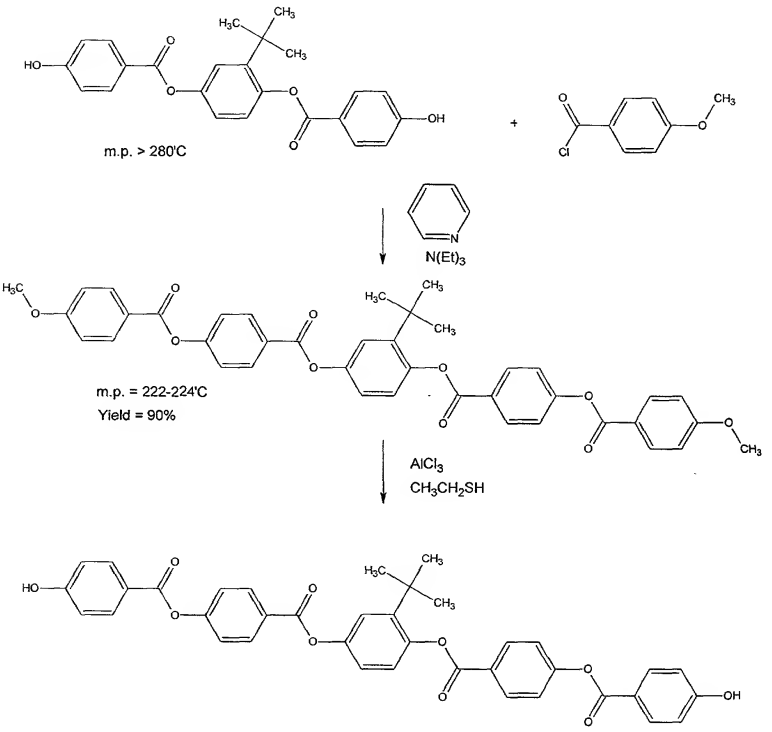
The reaction preferably is started under dry conditions at about 0 °C but can be allowed to warm to room temperature (~25 °C) as it proceeds. The reaction should not go above room temperature or ester cleavage can occur. The same procedure can be used to form diphenols with methyl, n-alkyl, halogen, and other groups substituted on the central aromatic ring.

Upon increasing methyl ether concentration to 35X the concentrations used by Node, the solubility limit of the product complex was exceeded, permitting the complex to crystallize out of the reaction mixture before the aromatic esters had an opportunity to cleave. Quantitative yields were obtained when the complex crystallized directly from the reaction mixture, effectively removing the molecule

from further reaction that would form side products:



The diphenolic platform mesogens can be lengthened by reacting additional 4-methoxy benzoyl chloride with bis 1,4 [4'-methoxybenzoyloxy] t-butylphenylene to produce the dimethoxy compound with four or five aromatic rings, depending upon the reactant ratios. Cleavage with Lewis acid and thiol produces the respective elongated diphenolic platform molecules:



The phenolic end group(s) are esterified by acyl chlorides, thus providing a route to polymerizable mesogens. For example, reaction of C0[H,TB,H](OH)$_2$ with methacryloyl chloride formed the monoester which was coupled to bifunctional

sebacoyl chloride to form an alkyl diester linked, methacrylate terminated liquid crystalline monomer, {C0[H,TB,H] (MeAcry)(O) }$_2$ (seb) with $T_{n->I}$ of 145°C and a T_g of 25°C. This monomer had no tendency to crystallize since the synthesis yielded three different isomers with differing mutual orientation of t-butyl groups. The material does have a high viscosity, however, making it somewhat inconvenient to process at room temperature, and thus T_g.

Dimers

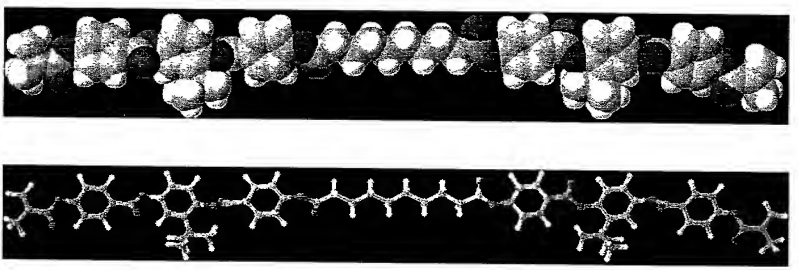
Preferred novel mesogens are mesogenic dimers. Some workers have noticed that non-reactive dimeric and polymeric derivatives of C6[H,TB,H] type mesogenic cores are much more unlikely to crystallize [S. Lee et al., Macromol., **27**(14), 3955 (1994)]. In order to make the dimer molecule, a second mesogenic, platform molecule, 1,4 [4'- hydroxybenzoyloxy] t-butylphenylene, C0[H,TB,H](OH)$_2$, was synthesized by coupling p-anisoyl chloride with t-butyl hydroquinone and then cleaving the methoxy end groups with a liquid alkane thiol, preferably ethanethiol, and aluminum chloride. This molecule can be further extended by reaction with p-anisoyl chloride and the same methoxy cleavage reaction. Fully aromatic diphenol terminated mesogens of any length can be thus produced.

Reaction of C0[H,TB,H](OH)$_2$ with a less than stoichiometric amount of methacryloyl chloride forms the monoester and diester. The monoester and diester are washed away from the diphenol starting material with methylene chloride and the monoester is separated from the diester as an insoluble solid by diluting the methylene chloride solution into hexane.

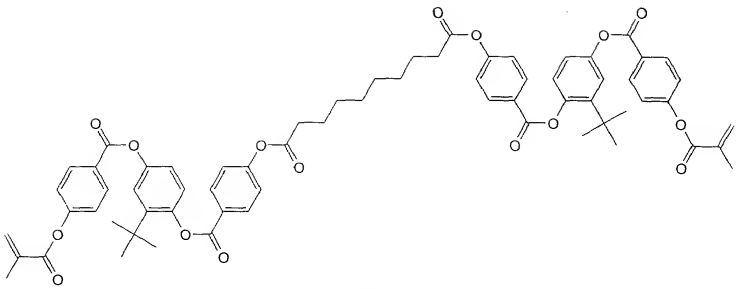
The monoester can be coupled to bifunctional sebacoyl chloride to form a alkyl diester linked, methacrylate terminated liquid crystalline monomer, {C0[H,TB,H]

(MeAcry)(O) }$_2$ (seb) with $T_{n->I}$ of 145°C and a T_g of 25°C. This monomer has no tendency to crystallize since the synthesis yields three different isomers with differing mutual orientation of t-butyl groups. However, the material is highly viscous, and processing close to room temperature, and thus T_g, is somewhat inconvenient.

The following is a ChemSketch 4 rendition of the minimum energy conformation of {C0[H,TB,H] (MeAcry)(O) }$_2$ (seb). As expected the most stable conformation is an extended form with a very high molecular length to width ratio which is likely to form high $T_{n->I}$ liquid crystal monomers.

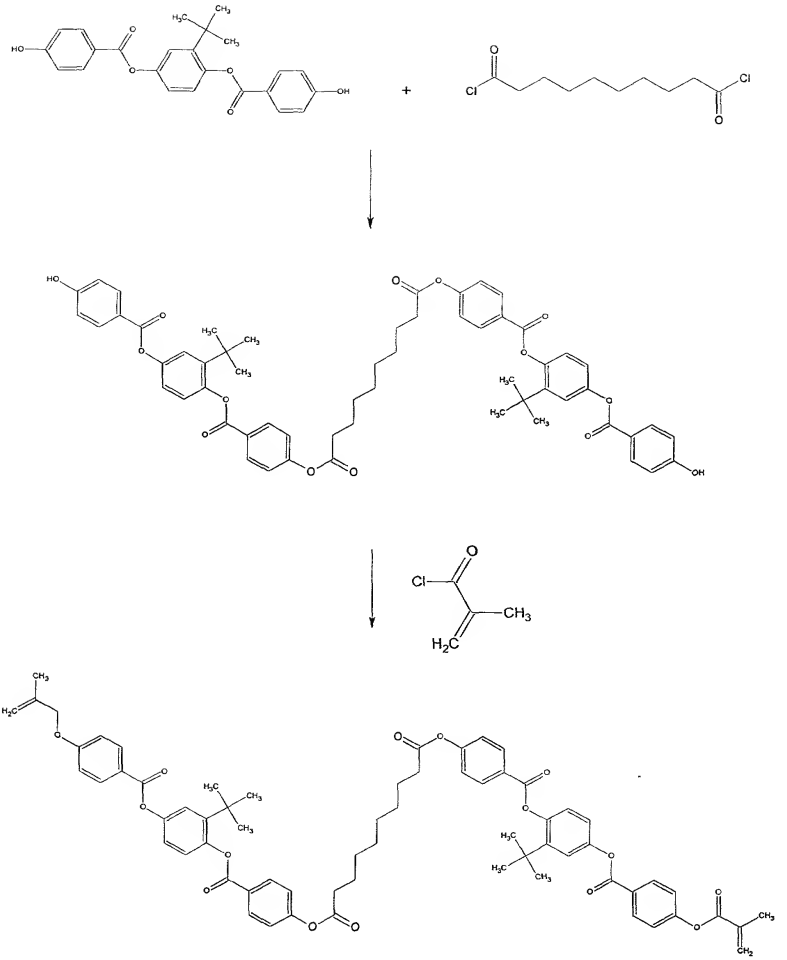


A minimum energy conformation of a preferred mesogenic dimer is decanedioic acid bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester {C0[H,TB,H] (MeAcry)(O) }$_2$ (seb):

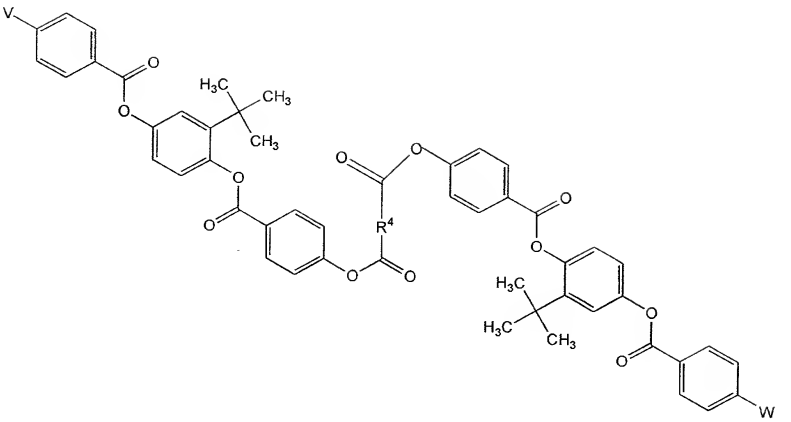


$C_{66}H_{66}O_{16}$
Exact Mass: 1114.44
Mol. Wt.: 1115.22
C, 71.08; H, 5.97; O, 22.95

Alternately, the partially or completely methacryloylated or acryloylated versions of decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester and decanedioic acid bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester are made as illustrated below:



The first reaction product in the above figure is a novel alkylenedioic bis-(4-{2-alkyl-4-[4-(hydroxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester having the following general structure:



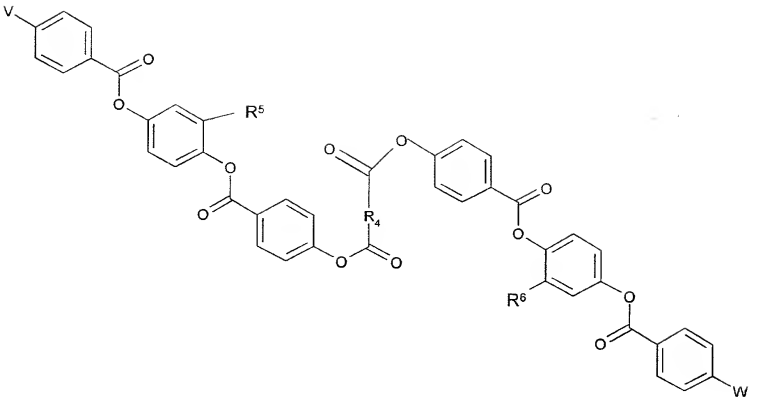
wherein

R^4 has from about 2 to about 20 carbon atoms, preferably from about 2 to about 12 carbon atoms, and most preferably from about 6 to about 12 carbon atoms.

the alkyl substituent on the central aromatic group of the aromatic ends includes, but is not necessarily limited to t-butyl groups, isopropyl groups, and secondary butyl groups. Most preferred are t-butyl groups; and,

V and W are selected from the group consisting of terminal functionalities and polymerizable groups. In platform molecules, V and W are terminal functionalities. In polymerizable mesogens, V and/or W are polymerizable groups.

The same procedures may be used to make mesogens having the following general structure:



wherein

R^5 and R^6 are selected from the group consisting of hydrogen, halogen, n-alkyl groups having from about 1 to 6 carbon atoms, aryl groups, and bulky organic groups; and,

V and W independently are selected from the groups comprising polymerizable groups and terminal functionalities.

Suitable terminal functionalities independently are selected from the group consisting of hydroxyl groups, amino groups, and sulfhydryl groups. Most preferred terminal functionalities are hydroxyl groups.

Suitable polymerizable groups may be polymerized by nucleophilic addition, free radical polymerization, or a combination thereof. Preferred polymerizable groups are polymerizable by Michael addition. Michael addition requires the addition of a nucleophile and an electron deficient alkene. Groups suitable for polymerization by Michael addition include but are not necessarily limited to the examples found in A.

Michael, *J. Prakt. Chem. [2] 35, 349 (1887)*; R. Connor and W. R. McClelland, *J. Org. Chem.*, **3**, 570 (1938); and C. R. Hauser, M. T. Tetenbaum, *J. Org. Chem.*, **23**, 1146 (1959), all of which are incorporated by reference herein.

Examples of suitable polymerizable groups include, but are not necessarily limited to substituted and unsubstituted alkenyl ester groups comprising a polymerizable unsaturated carbon-carbon bond, wherein said alkenyl group has from about 2 to about 12 carbon atoms, preferably from about 2 to about 9 carbon atoms, more preferably from about 2 to about 6 carbon atoms. Preferred alkenyl esters are acryloyl alkoxy groups, methacryloyloxy alkoxy groups, acryloyloxy groups, and methacryloyloxy groups. V and W may be the same or different, depending upon the application. In a preferred application--a dental application--V and W comprise terminal alkenyl groups.

These alkylenedioic bis-(4-{2-alkyl-4-[4-(hydroxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) esters are novel compounds, and may be used as "platform molecules," or polymerizable mesogens. A most preferred alkylenedioic bis-(4-{2-alkyl-4-[4-(hydroxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester is decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester.

In order to make the dihydroxyaromatic terminated mesogens, 1,4 bis(4'-hydroxybenzoyloxy) t-butylphenylene or bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy carbonyl}- phenyl) ester is dissolved in a solvent at a ratio of about 10 ml. solvent per gram. The material is dissolved in the solvent under an inert gas, preferably dry nitrogen. Suitable solvents are heterocyclic bases, with a preferred solvent being pyridine. This first mixture is diluted with a chlorinated organic

solvent, preferably methylene chloride, in an amount equal to the volume of pyridine.

A second mixture is formed by dissolving an alkyloyl chloride in a chlorinated organic solvent at a ratio of about 10 ml solvent per gram of alkyloyl chloride. A preferred chlorinated organic solvent is methylene chloride. The alkyloyl chloride comprises an alkyl portion having from about 2 to about 20 carbon atoms, preferably from about 6 to about 20 carbon atoms, more preferably from about 6 to about 12 carbon atoms, and most preferably is sebacoyl chloride. This second mixture includes at least some of benzoquinone inhibitor, suitable concentrations being from about 1 to about 100 ppm, with a preferred concentration being about 10 ppm. The second mixture is added slowly to the first mixture with stirring, preferably with a syringe through a suba seal. After about 24 hours at room temperature, a precipitate is seen. The solvent, preferably methylene chloride and pyridine, are pumped off.

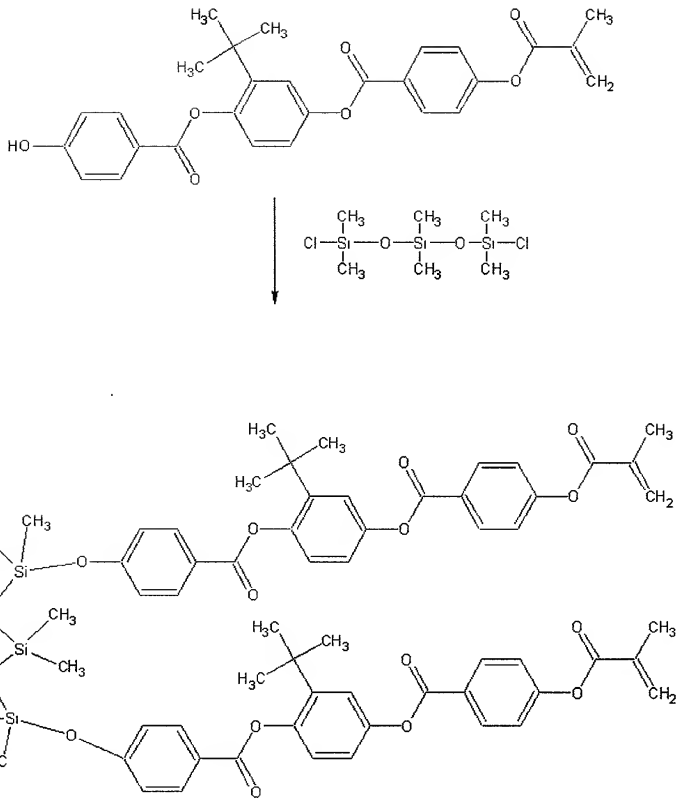
Any remaining pyridine is converted to a salt using a suitable acid, preferably hydrochloric acid, and the salt is removed by washing with water. Water is filtered off from the remaining white precipitate. Residual water is removed using a suitable solvent, preferably acetone, to dissolve the remaining precipitate, which is then stirred with a suitable amount of magnesium sulfate. The solution is dried down and a dissolved in a chlorinated organic solvent, preferably methylene chloride (DCM), is added to dissolve the solid. After 24 hours at room temperature the unreacted 1,4 bis(4'-hydroxybenoyloxy) t-butylphenylene crystallizes out of solution as a white precipitate and separated from the mixture. The solution was then placed in the freezer overnight and decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester precipitates out of solution. Silica and basic alumina may be added to absorb any remaining methacrylic acid or carboxylic

acid terminated products.

Aromatic terminated mesogens (herein called "mesogenic dimers"), such as the foregoing, are used as a diluent and blended with the aliphatic terminated mesogens (herein called polymerizable mesogen) to form the polymerizable mixture. The quantity of mesogenic dimer in the blend will vary depending upon the dimer and its impact on transition temperature, final product, etc.

-Reaction of dimethyl amine or dichloro terminated oligodimethylsiloxanes with the mono methacrylate ester of 1,4 [4'-hydroxybenzoyloxy] t-butylphenylene

Molecules with higher temperature stability can be prepared by reacting dimethyl amine or dichloro terminated oligodimethylsiloxanes with the mono methacrylate ester of 1,4 [4'-hydroxybenzoyloxy] t-butylphenylene, as shown below:



In this embodiment, the mesogenic platform molecule 1,4 [4'-hydroxybenzoyloxy] t-butylphenylene is further extended by reaction with p-anisoyl chloride and subsequent ether methyl group cleavage with aluminum chloride and ethane thiol. Fully aromatic diphenol terminated mesogens of any length can be thus produced. Reaction with acryloyl or methacryloyl chloride forms the monoester, which can be coupled to reactive aliphatic or siloxane oligomers to form polymerizable liquid crystals with reactive ends.

Formation of Alkoxy Terminal Functionalities

In order to produce alkoxy groups as terminal functionalities, an excess of anisoyl chloride is mixed with a desired 1,4 bis(4'-hydroxybenzoyl oxy)-R^2 phenylene, (preferably a t-butylphenylene) in an excess of pyridine and triethyl amine (about a 10:1 ratio) with stirring under nitrogen for several hours, preferably about 4hr. The pyridine is removed under vacuum, and the mixture is extracted into ethyl ether. Amine hydrochloride is removed by vacuum filtration and the remaining solids are washed with a suitable solvent, such as water and acetone. The product had a melting point of 222-224 °C and the structure of the molecule was confirmed by NMR to be the aromatic dimethoxy compound.

Low Polymerization Shrinkage

The mesogens exhibit "low polymerization shrinkage" preferably no more than 3 vol.% change, more preferably no more than about 2 volume percent change. Polymerization shrinkage is measured by codissolving the monomers in dichloromethane with 0.3 wt.% camphorquinone photoinitiator, 100 ppm benzoquinone and 1 wt.% N,N' dimethylaminoethyl methacrylate activator and subsequently pumping off the solvent, all under yellow light. The monomers are then

polymerized in film or droplet form in less than 1 minute by exposure to a dental curing light (Dentsply Spectrum Curing Lamp) with a significant output at 420 nm.

FTIR spectroscopy (Nicolet Magna-IR 560) is used to measure the degree of cure by observing the decrease in the 1637 cm^{-1} alkene band vs. the aromatic internal thickness band at 1603 cm^{-1}. Thin film measurements that avoid oxygen inhibition are performed by sandwiching the monomer between polyvinylidene chloride films, which have an optical window in the wavelength region of interest. The IR spectrum of solid droplets is evaluated using a single bounce reflectance measurement. The flat bottom surface of the droplet is pressed against the germanium lens of a Spectra Tech Thunderdome attachment.

Polymerization of the monomers can be observed between transparent polyvinylidene chloride films under cross-polarized optical microscopy in the heated stage of a Nikon Optimat microscope. Little change in the local birefringence and thus local orientation is noted upon polymerization at room temperature or upon heating to 180° C.

Fracture Toughness

Compact tension samples (ASTM E399) with known edge crack length are fabricated by photocuring the monomer with initiator and activator in silicone molds. After polishing the surface with 600 grit polishing agent and soaking in physiologic saline at 37 °C for 24 hours the samples were tested at room temperature under displacement control at 1mm/min until failure.

The fracture toughness of the crosslinked, amorphous glass suitable is about 0.4 MPa-$m^{1/2}$, preferably about 0.5 MPa-$m^{1/2}$, which is identical to that found for photocured, isotropic dimethacrylate based resins such as GTE resin.

Fillers

Considerable amounts of soluble impurity can be added to the polymerizable mesogens, or a mixture comprising the polymerizable mesogens, without changing the $T_{nematic->isotropic}$ transition temperature of the polymerizable mesogens. Thus, a high volume fraction of filler can be added to the polymerizable mesogens and still form a composite that maintains desirable, low viscosity flow and low polymerization shrinkage characteristics at temperatures of curing. Commercial products add up to about 70-80 wt% filler. A preferred embodiment uses about 30 wt.% filler.

A variety of fillers may be used. A preferred filler is amphoteric nano-sized metal oxide particles having a diameter in nanometers which is sufficiently small to provide transparency effective for photopolymerization but sufficiently large to provide effective fracture toughness after photopolymerization. Substantially any "metal" capable of forming an amphoteric metal oxide may be used to form the metal oxide particles. Suitable metallic elements include, but are not necessarily limited to niobium, indium, titanium, zinc, zirconium, tin, cerium, hafnium, tantalum, tungsten, and bismuth. Also suitable in place of the metal in the oxide is the semi-metallic compound, silicon. As used herein, unless otherwise indicated, the term "metal oxide" is defined to include silicon, and the word "metal," when used to refer to the metal oxide is intended to also refer to silicon.

The metal oxides may be made of a single metal, or may be a combination of metals, alone or combined with other impurities or "alloying" elements, including, but not necessarily limited to aluminum, phosphorus, gallium, germanium, barium, strontium, yttrium, antimony, and cesium.

A monomeric liquid crystal (LC) containing a high volume fraction of filler nanoparticles is a highly constrained system. As a result, at least for some monomeric species, both smectic and crystalline transitions should be suppressed. The consequent widening of the stability range of nematic mesophase should permit the composite to polymerize at much lower temperatures than in unfilled systems, resulting in lower polymerization shrinkage.

The metal oxide nanoparticles may be prepared using any known methods, such as "sol-gel" techniques, direct hydrolysis of metal alkoxides by water addition, forced hydrolysis of relatively low-cost metal salts, or non-hydrolytic reactions of metal alkoxides with metal halide salts. Examples of such procedures are shown in the following references, each of which is incorporated herein by reference: W. Stöber and A. Fink, J. of Colloid and Interface Science, v. 26, 62-69 (1968); M.Z.-C. Hu, M.T. Harris, and C.H. Byers, J. of Colloid and Interface Science, v. 198, 87-99 (1988); M. Ocaña and E. Matijević, J. of Materials Research, v. 5(5), 1083-1091 (1990); L. Lerot, F. LeGrand, P. de Bruycker, J. of Materials Science, v. 26, 2353-2358 (1991); H. Kumazawa, Y. Hori, and E. Sada, The Chemical Eng'g. Journal, v. 51, 129-133 (1993); S. K. Saha and P. Pramanik, J. of Non-Crystalline Solids, v. 159, 31-37 (1993); M. Andrianainarivelo, R. Corriu, D. Leclercq, P.H. Mutin, and A. Vioux, J. of Materials Chemistry, v. 6(10), 1665-1671 (1996); F. Garbassi, L. Balducci, R. Ungarelli, J. of Non-Crystalline Solids, v. 223, 190-199 (1998); J. Spatz, S. Mössmer, M. Mo[umlaut]ller, M. Kocher, D. Neher, and G. Wegner, Advanced Materials, v. 10(6), 473-475 (1998); R. F. de Farias, and C. Airoldi, J. of Colloid and Interface Science, v. 220, 255-259 (1999); T. J. Trentler, T. E. Denler, J. F. Bertone, A. Agrawal, and V.L. Colvin, J. of the Am. Chemical Soc., v. 121, 1613-1614 (1999);

Z. Zhan and H.C. Zheng, J. of Non-Crystalline Solids, v. 243, 26-38 (1999); M. Lade, H. Mays, J. Schmidt, R. Willumeit, and R. Schomäcker, Colloids and Surfaces A: Physiochemical and Eng'g Aspects, v. 163, 3-15 (2000); and the procedure described in "Sol-gel processing with inorganic metal salt precursors," authored by "Michael" Zhong Cheng Hu, licensable via Oak Ridge National Laboratory under ORNL control number ERID 0456.

The application will be better understood with reference to the following examples, which are illustrative only:

Example 1

Synthesis of 4-nitrophenylenecarbonyloxy 6'-hexane-1'-ol

60 g 4-nitrobenzoic acid (0.4 mole) was dissolved in 250 ml (2.07 mole) dry hexandiol that had been fused in the reaction vessel at 165 °C. 1 ml. tetrabutyltitanate catalyst was added, and the mixture was stirred for 3 hours at 135 °C before cooling to 95 °C where stirring was continued under dynamic vacuum for two days to remove the water of condensation.

The solution was extracted with 1 liter diethyl ether, centrifuged or filtered to remove the catalyst, and then washed two times with 500 ml 5% $NaHCO_3$ to remove unreacted acid and excess diol. After the ether was vacuum evaporated, the residue was dissolved in 150 ml boiling ethanol to which 75 ml water was added. Upon cooling to room temperature bis 1,6-(4 nitrophenylene carbonyloxy)hexane precipitated as 7.61 grams of a yellow powder (T_m = 112 °C).

The remaining solution was evaporated and redissolved in 150 ml diethyl ether to which was added 75 ml hexane. After crystallization at -20 °C 4-nitrophenylene 4-

carbonyloxy 6'-hexane-1'-ol (86.7 grams) was isolated (T_m=32-35 °C). NMR indicated that both of these products were greater than 98% purity.

Example 2

Synthesis of 4-(6-hydroxyhexyloxy)phenylenecarbonyloxy 6'-hexane 1'-ol

20 ml (0.166 mole) of dry, molten hexandiol was transferred to a flask with an attached short path distillation unit. 200 ml dry dimethylsulfoxide (DMSO) and then 40 ml of 1M KOBu^t was then added to the diol and stirred 45 minutes at room temperature. The Bu^{t}OH and a small amount of DMSO were distilled off under vacuum between 25-50 °C over one hour. 8ml (0.04 mole) of dry 4-nitrophenylenecarbonyloxy 6'-hexane-1'-ol was added producing a bright blue color that converted to a yellow coloration after 2 hours.

After stirring overnight, the DMSO and excess hexanediol was removed by vacuum distillation at 90 °C, whereupon the residue was taken up in 200 ml diethyl ether which was washed twice with 200 ml 5% $NaHCO_3$ and dried with $MgSO_4$. After the ether was distilled away, the solid was dissolved in a minimum amount of boiling ethanol and crystallized at -20°C. A 75-90% yield of the desired white product was obtained (T_m =30-33°C).

Example 3

Synthesis of 4-[6-hydroxyhexyloxy] benzoic acid

1.2 g (0.0037 mole) 4-(6-hydroxyhexyloxy)phenylenecarboxyoxy 6'-hexane 1'-ol was heated for 8 hours at 90 °C in a solution of 0.29 g (0.0074 mole) NaOH in 4 ml water. 20 ml of water was added to the clear solution and 0.3 ml of concentrated HCl added to precipitate the acid at pH=3-5. The white solid was filtered off and dried

under vacuum to produce a quantitative yield of the substituted benzoic acid (T_m=117°C).

Example 4

Synthesis of 4 (6'-chlorohexyloxy) benzoyl chloride

A three times molar excess of thionyl chloride (55ml) in toluene (300ml) was dropwise added over 20 minutes to 4-(6'-hydroxyhexyloxy)benzoic acid (60g, 0.252 mole) suspended in toluene (600ml) with a stoichiometric amount of pyridine (42 ml) at 0 °C. The suspension was continuously stirred for another 8 hours at room temperature, whereupon the toluene and excess thionyl chloride were distilled off at 70-100 °C with a slight nitrogen flow. The remaining slush of the pyridine hydrochloride and product was extracted with 1l boiling hexane and mixed with 5 g basic alumina and 5g neutral silica and filtered hot. A 90% yield of a very light yellow 4-(6'-chlorohexyloxy)benzoyl chloride liquid was obtained after evaporation of the hexane (T_m <20°C).

Example 5

Synthesis of bis 1,4 [4"-(6'-chlorohexyloxy)benzoyloxy] t-butylphenylene

65g of 4-(6'-chlorohexyoxy)benzoyl chloride (0.23 mole) was added to 16.75 g (0.1 mole) of t-butyl hydroquinone dissolved in 800 ml dry diethyl ether. 10 ml pyridine and 32 ml triethylamine were then added to this mixture. After stirring for 20 hours, the ether was filtered and washed two times with 200 ml 0.1N HCl and 200 ml saturated NaCl solution. The ether solution was then mixed with 10g basic alumina to remove unreacted acid and 10 g neutral silica to flocculate the suspension and dried over magnesium sulfate. The product starts to crystallize from the ether when the solution is reduced by half. After continued crystallization at –20 °C

overnight 63 g of product melting at 95-100 °C could be obtained. Another crop of crystals was obtained by further reducing the solution and crystallizing at -20°C over one week. NMR purity was >99%.

Example 6

Synthesis of bis 1,4 [4"-(6'-iodohexyloxy)benzoyloxy] t-butylphenylene

1.15 g (0.0016 mole) bis 1,4 [4"-(6'-chlorohexyloxy)benzoyloxy] t-butylphenylene dissolved in 20 ml acetone was boiled under nitrogen with 8.0 g NaI in 20 ml acetone for 20 hours. A quantitative yield of bis 1,4 [4"-(6'-iodohexyloxy)benzoyloxy] t-butylphenylene was obtained. The material melted at 76 °C and was >99% pure by NMR.

Example 7

Synthesis of bis 1,4 [4"-(6'-hydroxyhexyloxy)benzoyloxy] t-butylphenylene

36 g of bis 1,4 [4"-(6'-chlorohexyloxy)benzoyloxy] t-butylphenylene was dissolved in 750 ml of n-methypyrrolidinone (NMP) in a single neck flask. 15g KBr and 120 ml water were then added. The flask was then wired shut with a suba seal, and the solution was heated to 120 °C for 24 hours. Upon cooling, the solution was quenched into 1500 ml water and extracted with 250 ml methylene chloride. After evaporation of the methylene chloride, the solid was extracted with 1l of ether and washed with 1l water and dried with $MgSO_4$. The solution was concentrated and crystallized at –20 °C for 3 days to yield 17 g of white product melting at 80 °C. Additional product crystallized from the solution after several weeks. NMR purity was >99%.

Stopping the above reaction at intermediate times yielded mixtures of di-OH terminated, and asymmetric monochloro, monohydroxy compounds.

Example 8

Synthesis of bis 1,4 [4"-(6'-methacryloyloxyhexyloxy)benzoyloxy] t-butylphenylene

10 g (0.0165 mole) bis 1,4 [4"-(6'-hydroxyhexyloxy)benzoyloxy] t-butylphenylene was dissolved in 200 ml dry methylene chloride containing 100 ppm benzoquinone (free radical quencher). After cooling the above solution to 0 °C 3.2 ml (0.035 mole) distilled methacryloyl chloride was then added along with 3 ml (0.037 mole) pyridine and the solution was stirred for 24 hours in a sealed flask making no attempt to remove air from the solvent.

The solvent was vacuum evaporated and the resultant solid taken up in 250 ml ether and washed with 250 ml 0.1N H Cl and 250 ml saturated NaCl. After drying with $MgSO_4$ and filtering, the solvent was evaporated to yield 10 g of the desired product as a nematic liquid, which was >98% pure by NMR. This material could be crystallized from diethyl ether at –20 °C to form a white crystalline solid melting at 57 °C.

Example 9

Synthesis of bis 1,4 [4"-(6'-Z-hexyloxy)benzoyloxy] t-butylphenylene, Z=46mole%OH, 54mole% methacryloxy

10 g (0.0165 mole) of bis 1,4 [4"-(6'-hydroxyhexyloxy)benzoyloxy] t-butylphenylene was dissolved in 200 ml dry methylene chloride containing 100 ppm benzoquinone (free radical quencher). After cooling the above solution to 0 °C 1.75 ml (0.018 mole) distilled methacryloyl chloride was then added along with 1.5 ml (0.018 mole) pyridine, and the solution was stirred for 24 hours in a sealed flask making no attempt to remove air from the solvent.

The solvent was vacuum-evaporated and the resultant solid taken up in 250 ml ether and washed with 250 ml 0.1N HCl and 250 ml saturated NaCl. After drying with $MgSO_4$ and filtering, the solvent was evaporated to yield 10 g of the desired product as a nematic liquid, which was 54 mole% methacryloxy and 46 mole % hydroxyterminated by NMR. This material could be not be crystallized even after prolonged storage at –20 °C.

Liquid crystal monomers containing a variation in the OH substitution by functional groups could be made by adapting the above synthesis with an appropriate amount of methacryloyl or acryloyl chloride.

Example 10

Synthesis of bis 1,4 [4"-(6'-cinnamoyloxyhexyloxy)benzoyloxy] t-butylphenylene

5 g (0.0825 mole) of bis 1,4 [4"-(6'-hydroxyhexyloxy)benzoyloxy] t-butylphenylene was dissolved in 100 ml dry methylene chloride containing 100 ppm benzoquinone (free radical quencher). After cooling the above solution to 0 °C, 3.0 g (0.018mole) cinnamoyl chloride was then added along with 1.4 ml (0.017 mole) pyridine, and the solution was stirred for 24 hours in a sealed flask making no attempt to remove air from the solvent.

The solvent was vacuum-evaporated and the resultant solid taken up in 100 ml ether and washed with100 ml 0.1N HCl and 250 ml saturated NaCl. After drying with $MgSO_4$ and filtering, the solvent was evaporated to yield 5 g of the desired product which was >98% pure by NMR. This material could be crystallized from diethyl ether at –20 °C to form a white crystalline solid melting at 70 °C.

Example 11

Synthesis of bis 1,4 [4"-(6'-acetoxyoxyhexyloxy)benzoyloxy] t-butylphenylene

1 g (0.0165 mole) of bis 1,4 [4"-(6'-hydroxyhexyloxy)benzoyloxy] t-butylphenylene was dissolved in 20 ml dry methylene chloride. After cooling the above solution to 0°C, 0.27 ml (0.0037 mole) acetyl chloride was then added along with 0.3 ml pyridine, and the solution was stirred for 24 hours in a sealed flask.

The solvent was vacuum-evaporated and the resultant solid taken up in 20 ml ether and washed with 20 ml 0.1N HCl and 250 ml saturated NaCl. After drying with $MgSO_4$ and filtering, the solvent was evaporated to yield the product quantitatively at >98% purity by NMR. This material could be crystallized from diethyl ether at –20 °C to form a white crystalline solid melting at 82 °C.

Example 12

Synthesis of 1,4 Bis(4'-methoxybenzoyloxy)t-butylphenylene

Anisoyl chloride (4.93 g, 0.029 mole), t-butyl hydroquinone (2.00 g, 0.012 mole) in pyridine (50 ml) and triethyl amine (3.2 ml) were stirred under nitrogen for 4 hours with the mixture eventually becoming dark orange/red. The pyridine was removed under vacuum and the mixture was precipitated into ethyl ether (500 ml). Amine hydrochloride precipitated out of solution and was removed by vacuum filtration. The ether was evaporated and the slightly yellow crystals were dissolved in chloroform and extracted with slightly acidified water. The color of the crystals was then removed by stirring over basic alumina and the crystals were then purified by recrystallization in isopropanol. 4.8 grams of material was collected (88% yield) with a melting point of 138-140 °C. The structure of the molecule was confirmed by NMR.

Example 13

Synthesis of 1,4 Bis(4'-hydroxybenzoyloxy) t-butylphenylene

1,4 Bis(4-methoxybenzoyloxy) t-butylphenylene (0.5 g., 0.00115 mole) and aluminum chloride (1.23 g., 0.00921 mole) were added to ethane thiol (2.5 ml) and dichloromethane (2.5 ml) to form a slightly yellow solution. This mixture was stirred for 1 hour and a white solid precipitated out of solution during this time. The mixture was precipitated into 200 ml of water and extracted with ethyl ether. The ether was evaporated and 0.432 grams were recovered, (92% yield). The melting point was not determined, but was found in be in excess of 280 °C.

Example14

Synthesis of 1,4 Bis(4"-(4'-methoxybenzoyloxy)benzoyloxy)t-butylphenylene

The dark orange solution of anisoyl chloride (0.357 g, 2.096 mmole), 1,4 Bis(4'-methoxybenzoyloxy) t-butylphenylene (0.355 g, 0.873 mmole) in pyridine (25 ml) and triethyl amine (0.5 ml) were stirred under nitrogen for 4hr. The pyridine was removed under vacuum, and the mixture was extracted into ethyl ether (200 ml). Amine hydrochloride and the product were insoluble and were removed by vacuum filtration. The amine hydrochloride was removed by washing the solids with water and acetone. The product had a melting point of 222-224 °C and the structure of the molecule was confirmed by NMR.

Example 15

Synthesis of 1,4 Bis(4'-methacryloylbenzoyloxy) t-butyphenylene and 1-(hydroxybenzoyloxy),4-(4'-methacryloylbenzoyloxy) t-butylphenylene

0.2 g (4.92×10^{-4} mole) 1,4 bis(4'-hydroxybenzoyloxy) t-butylphenylene was dissolved in 1 ml pyridine containing 10 ppm benzophenone, and to this was slowly

added 0.026 ml (2.46×10^{-4} mole) methacryloyl chloride dissolved in 2 ml methylene chloride. After stirring for 12 hours at room temperature, the methylene chloride was pumped off and the remaining pyridine solution was diluted into 0.1 N HCl to neutralize the pyridine and precipitate the product. After washing the precipitate with water and drying under vacuum, the precipitate was taken up into ether and dried with $MgSO_4$. After ether evaporation, the suspension was taken up into 3 ml methylene chloride in which the starting diphenol was insoluble. After filtering away the diphenol, the monomethacrylate ($T_m = 230$ °C) was crystallized from the remaining solution at room temperature by the addition of 3ml hexane. The remaining clear solution contained mainly the dimethacrylate in very small amounts ($T_m = 142$°C).

Example 16

Synthesis of bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester {C0[H,TB,H] (MeAcry)(O) }$_2$

In order to make decanedioic acid bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester {C0[H,TB,H] (MeAcry)(O) }$_2$ (seb), 0.95g, 1.95mmole of 1-(hydroxybenzoyloxy),4-(4'-methacryloylbenzoyloxy) t-butylphenylene was dissolved in 10 ml dry pyridine under dry nitrogen and then diluted with 20 ml dry methylene chloride. 0.233g sebacoyl chloride (0.975mmol) was dissolved in 10 ml dry methylene chloride containing 10ppm benzoquinone inhibitor and added slowly with syringe through a suba seal into the first solution with stirring. After 29 hours at room temperature a small amount of precipitate was seen and the methylene chloride was pumped off and 0.01g paradimethylaminopyridine was added as a catalyst to continue the reaction.

After another 24 hours at room temperature, some unconverted phenol was still observed by TLC and 0.5ml methacryloyl chloride was dissolved in 10 ml dry methylene chloride and added to the reaction mixture to react any unconverted starting material to the dimethacrylate. After 3 hours the phenol had been completely converted and methylene chloride was removed under vacuum.

100ml of water containing 7.5ml concentrated HCl was added to the flask with stirring and stirred for four hours to remove the pyridine as the hydrochloride salt (pH=4). The water layer could be poured from the white layer which stuck to the walls of the vessel. After washing once more with deionized water, 100ml methylene chloride was added to dissolve the solid and the resulting organic phase was transferred to a separatory funnel and washed twice with 100ml brine saturated water and dried with magnesium sulfate. One gram each of silica and basic alumina were added to absorb any remaining methacrylic acid or carboxylic acid terminated products.

After standing for 8 hours the methylene chloride solution was filtered and added to 500ml of stirred hexane. After 8 hours the pure precipitated product was collected; the supernatent contained methacrylated starting material.

The white precipitate eluted in 80/20 ether/hexane on silica as a major spot and a very faint following spot. NMR revealed about 95% purity of the desired product (30% yield) with the rest being a methoxy terminated product which was carried over from the diphenol starting material. Solutions could be cast into a translucent, nematic glass at room temperature which gradually softened upon heating.

Example 17

Synthesis of Decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester

18.25g, (44.9mmole) of 1,4 bis(4'-hydroxybenzoyloxy) t-butylphenylene was dissolved in 120 ml dry pyridine under dry nitrogen and then diluted with 100 ml dry methylene chloride. 1.34g sebacoyl chloride (5.60mmol) was dissolved in 20 ml dry methylene chloride and added slowly with syringe through a suba seal into the first solution with stirring. After 24 hours at room temperature a small amount of precipitate was seen and the methylene chloride and pyridine were pumped off

300ml of water containing 7.5ml concentrated HCl was added to the flask with stirring and stirred for four hours to remove the pyridine as the hydrochloride salt (pH=4). The water was filtered off from the white precipitate that formed in the vessel. 200ml of acetone was added to dissolve the mixture which was then stirred with 3 grams of magnesium sulfate to remove any remaining water, after which the solution was dried down. 200ml methylene chloride (DCM) was added to dissolve the solid. After 24 hours at room temperature the unreacted 1,4 bis(4'-hydroxybenoyloxy) t-butylphenylene crystallized out of solution as a white precipitate. The solution was then placed in the freezer overnight and decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester precipitated out of solution.

The white precipitate eluted in 90/10 DCM/acetone on silica as a major spot and a very faint spots resulting from higher order polymerization. The product had a high NMR purity (>95%)..

Example 18

Synthesis of Decanedioic acid bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester

0.85g, (0.868mmole) of decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxycarbonyl}-phenyl) ester was dissolved in 20ml dry pyridine under dry nitrogen and then diluted with 20ml dry methylene chloride. 0.118g methacrylol chloride (1.13mmol) was dissolved in 10 ml dry methylene chloride containing 10ppm benzoquinone inhibitor and added slowly with syringe through a suba seal into the first solution with stirring. After 24 hours at room temperature a small amount of precipitate was seen and the methylene chloride and pyridine were pumped off.

100ml of water containing 1.0ml concentrated HCl was added to the flask with stirring and stirred for two hours to remove the pyridine as the hydrochloride salt (pH=4). The water layer could be poured from the white layer, which stuck to the walls of the vessel. After washing once more with deionized water. 50ml methylene chloride was added to dissolve the solid and the resulting organic phase was transferred to a separatory funnel and washed twice with 100ml brine saturated water and dried with magnesium sulfate. One gram each of silica and basic alumina were added to absorb any remaining methacrylic acid or carboxylic acid terminated products. NMR revealed that the product was the desired dialkene terminated monomer.

Persons of ordinary skill in the art will recognize that many modifications may be made to the present invention without departing from the spirit and scope of the present invention. The embodiment described herein is meant to be illustrative only

and should not be taken as limiting the invention, which is defined in the following claims.